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The effects of phase fractionation on the composition of oils, condensates and gases

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Abstract

The effects of phase fractionation on the composition of oils, condensates and gases have been studied in the laboratory by a differential evaporation experiment. The experiment was designed to simulate the behaviour of a single-charge petroleum during (upward) migration or in a reservoir undergoing uplift, scenarios thought to be typical for the Norwegian continental shelf. After each pressure reduction step, samples from all phases (oil, condensate, free and associated gas) were collected and analysed. The results show that, in general, small molecules are preferentially enriched in the gas phase, both at elevated pressure and temperature and under standard conditions (15°C, 1 bar). The solvent power of the gas phase for large molecules is drastically reduced at lower pressures (here below approx. 300 bar). Carbon isotope ratios of individual compound are not affected, while variations in isotope ratios of fractions can be explained by changes in the fraction compositions. Individual geochemical parameters behave as can be expected based on the molecular size and structure of the compounds involved. However, a generally valid, quantitative prediction of how geochemical parameters vary as a result of phase fractionation is very difficult, as this will depend not only on the pressure and temperature of fractionation, but also on the composition and amounts of the oil and gas that are involved. The observations from this study confirm the importance of phase fractionation as an important process to consider when interpreting geochemical data for both condensates and oils. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Phase fractionation; Oil; Gas condensate; Differential evaporation; Gas–liquid equilibrium; Molecular fractionation

1. Introduction

Phase fractionation is one of the processes by which gas-condensates[1] can be generated in the subsurface, either during migration or in a reservoir (Zhuze and Ushakova, 1981; England and Mackenzie, 1989; Larter, 1990). Petroleum is generally thought to be expelled from its source rock as a single-phase fluid and will normally migrate towards shallower depths with lower temperatures and pressures. At depths where the pressure drops below the bubble point of the petroleum, separate oil and gas phases can be formed, which can potentially follow different migration paths and end up in different reservoirs. Phase fractionation can also occur in reservoirs due to pressure reduction (uplift or leakage) or the addition of (dry) gas to an oil-filled reservoir, as the new mixture will have a higher bubble point than the original oil. Subsequent remigration of the oil and/or gas phase can result in the presence of several reservoirs filled with petroleum from a common source but with different compositions. It is important to recognise the effects of these physical phase fractionation processes and to distinguish them from other processes controlling petroleum composition, such as variations in source rock type and thermal maturity level. Only in this way can reliable correlations between oils, condensates and source rocks be carried out and a good understanding of the petroleum geology be obtained.

The changes in petroleum composition introduced by liquid-to-gas transitions can be studied in the

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[1] Condensate (sometimes referred to as gas-condensate) is that part of petroleum, which is present in the gas phase in a reservoir, but precipitates as a liquid during protection due to the reduction in temperature and pressure.

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laboratory under controlled temperature and pressure conditions. Such experiments are routinely performed in PVT laboratories to study the behaviour of petroleum reservoirs during production. These so-called differential evaporation experiments (Fig. 1) start with a sample of single-phase reservoir fluid at the pressure and temperature of the reservoir. Subsequently, the pressure is reduced to below the bubble point giving a gas and a liquid phase. The gas phase is removed and transferred to standard temperature and pressure (15°C, 1 atm) via a "single flash" yielding "free" gas[2] and condensate. The remaining liquid phase (at high p, T) is subjected to a next stage of pressure reduction, etc. If a sample of the liquid phase is collected, this will yield oil and associated gas after single flash to standard conditions.

Several laboratory experiments with gas–oil transitions have been described in the literature (Price et al., 1983; Thompson 1987, 1988; England et al., 1991; Larter and Mills, 1991; Carpentier et al., 1996). Much of this work, particularly by Thompson, focussed on the light hydrocarbon fraction (C_6–C_8). Data on the $C_{15}+$ fraction has been reported (e.g. Larter and Mills, 1991), but not very comprehensively, while the gas fraction (C_1–C_5) has been largely ignored. The aim of our experiment was to complement the published work by studying the full range of changes occurring during phase fractionation. This was obtained by sampling all gas and liquid phases during each stage of a differential evaporation experiment and subjecting these samples to a broad range of geochemical analyses. It was our intention to use the results from these experiments to set up general guidelines for how geochemical parameters may change due to phase fractionation. In contrast to the earlier reported laboratory studies, which were started with "artificial" reservoir fluids, composed of an oil and a non-related gas, the starting liquid in our experiment consists of a naturally occurring reservoir fluid. The experiments were intended to simulate a typical scenario on the Norwegian continental shelf, i.e. upward migration or reservoir uplift of a single-charge petroleum, rather than e.g. gas flushing as may be more common elsewhere. The experiment was carried out under realistic pressures (corresponding to depths of approx. 5000 m and less) while the (isothermal) temperature conditions only represent the deeper reservoir interval and not the cooler, shallower layers.

2. Experimental

A modified differential evaporation experiment was set up in Statoil's Fluid Laboratories. The starting volume of reservoir fluid was increased compared to the routine set-up in order to obtain a sample of every phase (oil, associated gas, condensate, free gas) from each stage. In routine experiments the liquid phase is not sampled during each stage in order to obtain a good mass balance. However, in our experiment small aliquots of the liquid phase were collected during each stage in the modified experiment. Finally, the number of

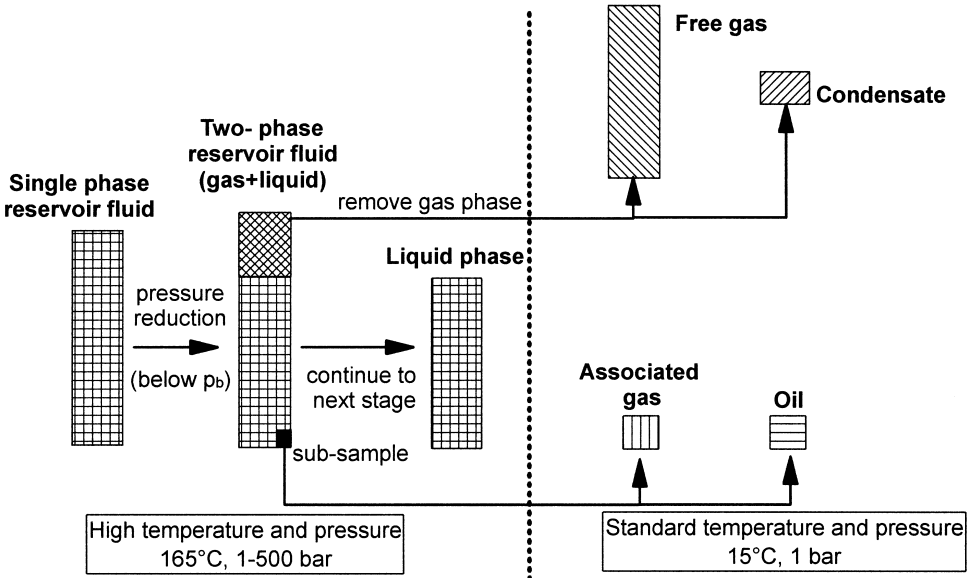

Fig. 1. Schematic overview of differential evaporation experiment. p_6 = bubble point.

[2] This gas phase is termed "free gas" throughout this report in order to distinguish it from the (oil-)associated gas that is also obtained.

stages and the associated pressures were selected to give reasonable size samples for all phases.

The experiment was carried out with a bottom hole sample (BHS), collected at reservoir conditions (494.8 bar, 164.8°C) from a well offshore mid Norway. Under reservoir conditions this is a single-phase fluid with a gas–oil ratio (GOR) of 390 Sm^3 gas/Sm^3 oil and a bubble point pressure of 412 bar. During the experiment the pressure was reduced from reservoir pressure to 1 bar in six stages: 390, 340, 280, 200, 100 and 1 bar; all at 164.8°C. In a geological setting, these pressures would be compatible with depths ranging from approximately 3900 m to surface (assuming hydrostatic conditions). Obviously, the constant high temperature deviates from a normal geological situation, where temperature and pressure will decrease simultaneously. However, careful evaluation of the results strongly suggests that the constant temperature does not significantly alter the results, with the exception of the last stage with a pressure reduction to 1 bar (see discussion below).

At each stage the gas phase was removed and a small sample of the liquid phase (approx. 3 ml, 7–10% of the remaining liquid phase) was taken before the next stage of pressure reduction was carried out. These liquid and gas samples were collected at the elevated experimental temperature and pressure. After collection, they were transferred to standard conditions (1 bar, 15°C) via a single flash, thus yielding stabilised oil, associated gas, condensate and free gas. All four sample types were obtained from every stage, apart from the last stage (no. 6) as a "single flash" of oil from 1 bar/164.8°C to 1 bar/15°C obviously does not produce an associated gas. Some of the samples obtained (associated gas and condensate from stage 5) were very small and the analytical program could only partly be carried out.

Gas samples were analysed by gas chromatography for the distribution of C_1–$C_{10}+$ components, while isotopic measurements were performed on CO_2 and the C_1–C_5 hydrocarbons. Oils and condensates were subjected to the following analytical program: whole-fluid GC including quantification of the light hydrocarbon fraction, gross composition analysis by thin layer chromatography (Iatroscan), GC and GCMS analysis of the saturated and aromatic hydrocarbon fractions, and carbon isotope measurements of the whole oils/condensates and all fractions. All analyses were performed in accordance with "The Norwegian Industry Guide to Organic Geochemical Analyses" (NIGOGA, 1993).

3. Results and discussion

3.1. Overall mass balance and bulk fluid composition

Based on the weights of all samples collected during the various stages, a mass balance has been set up for the experiment (Table 1). Gas–oil ratios (GOR) have been calculated for the gas phase (= free gas/condensate), the liquid phase (= associated gas/oil), and for the whole system (free + associated gas/oil + condensate).

Between 8 and 14% of the liquid was evaporated during each stage (Fig. 2). The bulk of this material is represented by the free gas (4–9%), with condensate (0.3–2.4%; 5.6% in Stage 6) accounting for the rest. The residual oil after Stage 6 represents 59% of the starting material (after correction for liquid samples removed during the experiment). During all stages a total of 22265 ml gas (free and associated) were liberated from the oil. This is equivalent to an overall GOR of 404 Sm^3/Sm^3, which is in good agreement with a GOR of 390 Sm^3/Sm^3 that was measured in a single flash experiment.

GORs have been calculated for the entire system, the gas phase and the liquid phase (Fig. 3). GORs for the liquid phase gradually decrease from 376 at Stage 1 to 57 at Stage 5 (no associated gas is released during Stage 6). GORs for the gas phase are much higher and increase from 1840 at Stage 1 to 18293 at Stage 5, with a low value of 829 at Stage 6. The latter is due to combination of high temperature (165°C) and low pressure (1 bar) which causes a transfer of low-boiling (C_6–C_9) components to the gas phase. The GOR of the entire system parallels the GOR of the liquid phase, reflecting the quantitative dominance of the latter over the gas phase.

The quantitative dominance of the oil phase throughout the experiment, as described in the mass balance, makes that any changes in the oil phase during a single stage are expected to be small, especially with regard to bulk parameters (effects on the gasoline-range components can be significant), even though the released condensate may have a significantly different composition. However, small differences during each stage may amount to a significant cumulative effect on oil composition over the entire differential evaporation experiment. The composition of the associated gas can change significantly throughout the experiment as the whole fraction eventually is converted to free gas.

A similar experiment was performed by Larter and Mills (1991). Their starting fluid was an artificial gas-condensate with a GOR of 3700 Sm^3/Sm^3. Although they do not report a mass balance, this higher initial GOR may give rise to quantitatively different effects compared to our experiment, as the relative sizes of the phases will be very important in determining the extent of any gas–liquid phase fractionation effects.

Condensate–gas ratios (CGR; mass of condensate/mass of free gas) have been calculated for the gas phase of each stage (Fig. 3). They show an exponential decrease with decreasing pressures throughout the experiment before ending with a high value in Stage 6

Table 1
Differential evaporation experiment: mass balance[a]

Stage	Pressure (bar)	Material removed (at standard pressure and temperature, 1 bar, 15°C)								Liquid phase transferred to next stage[b] (g)
		Free gas		Condensate		Oil		Associated gas		
		Volume (ml)	Density (g/cm3)	Weight (g)	Density (g/cm^3)	Weight (g)	Density (g/cm^3)	Volume (ml)	Density (mg/cm^3)	
Start	495									70.40
Stage 1	390	2958	0.812	1.302	0.810	2.993	0.856	1314	0.855	61.78
Stage 2	340	5414	0.810	1.455	0.805	2.746	0.856	871	0.872	51.27
Stage 3	280	3421	0.819	0.507	0.801	2.552	0.856	594	0.888	44.13
Stage 4	200	2738	0.807	0.232	0.790	3.534	0.856	412	0.931	38.00
Stage 5	100	2352	0.838	0.099	0.770	2.720	0.856	234	1.009	31.66
Stage 6	1	1957	1.085	1.773	0.751	27.286	0.872	0	–	–

Stage	Pressure (bar)	Oil		Associated gas		Condensate		Free gas		Gas to oil ratio (GOR) (Sm^3/Sm^3)		
										Associated gas	Free gas	Association +free gas
		Vol. (ml)	wt. (g)	vol. (ml)	wt. (g)	vol. (ml)	wt. (g)	vol. (ml)	wt. (g)	Oil	Condensate	Oil +condensate
Start	495		70.40									390.4[c]
Stage 1	390	52.92	45.30	19889	20.85	1.61	1.30	2958	2.94	376	1840	419
Stage 2	340	47.94	41.04	13016	13.91	1.81	1.46	5414	5.38	272	2995	370
Stage 3	280	44.11	37.76	8789	9.57	0.63	0.51	3421	3.44	199	5405	273
Stage 4	200	41.03	35.12	5320	6.07	0.29	0.23	2738	2.71	130	9323	195
Stage 5	100	38.32	32.80	2172	2.69	0.13	0.10	2352	2.42	57	18293	118
Stage 6	1	31.29	27.29	0	0	2.36	1.77	1957	2.60	0	829	58

[a] Actual weights and volumes of fractions obtained during the experiment are listed in the upper part of the table. The lower part contains a mass balance for each stage, assuming full conversion of the liquid phase (oil and associated gas) to standard condtions.
[b] Calculated from the sum of the fractions in the following stage
[c] Measured in a single flash of reservoir fluid (495 bar, 165°C) to standard conditions (1 bar, 15°C).

(temperature effect, see above). This exponential trend is different from the linear relationship between CGR and pressure that was reported by England et al. (1991). The difference can partly be explained by the fact that England and co-workers measured how much oil of a given composition could be dissolved by a gas of fixed composition, while the composition of both liquid and gas phases vary continuously in our experiment.

The whole fluid composition of all samples, expressed as relative concentrations of C_1–C_{10}+ pseudo-components (Table 2), is shown in Fig. 4. Oils comprise 85–90% C_{10}+ components and change very little during most of the experiment (up to Stage 5). Condensates, on the other hand, show a gradual change towards lower proportions of C_{10}+ at lower pressures, starting at 75% in Stage 1 and decreasing to 60% in Stage 4.[3] This change reflects the lower ''solvent power'' of the gas phase for large molecules at lower pressures. The amount of C_{10}+ components is strongly reduced to 20% in the Stage 6 condensate. At the low pressure during this stage (1 bar) the geologically unrealistically high temperature (165°C) is above the boiling point of components up to C_9 and will cause a massive transfer of the C_1–C_9 fraction to the gas phase and most of the C_5–C_9 part of this material will end up in the condensate after cooling to 15°C (standard p, T). In comparison, at 100 bar (Stage 5) the boiling point of propane (C_3) is approx. 160°C, which means that compounds larger than propane will predominantly be present in the liquid phase. During Stages 1 through 5 the release of condensate with a different composition does not significantly alter the composition of the remaining oil as the amount of condensate is small and it contains only a modest amount of C_6–C_9 components. During Stage 6 a fairly large amount of condensate is generated, which, in combination with its large proportion of C_6–C_9 components, significantly affects the composition of the remaining oil. However, as pointed out earlier, Stage 6

[3] The composition of the condensate from the Stage 5 is considered to be unreliable due to the very small sample size.

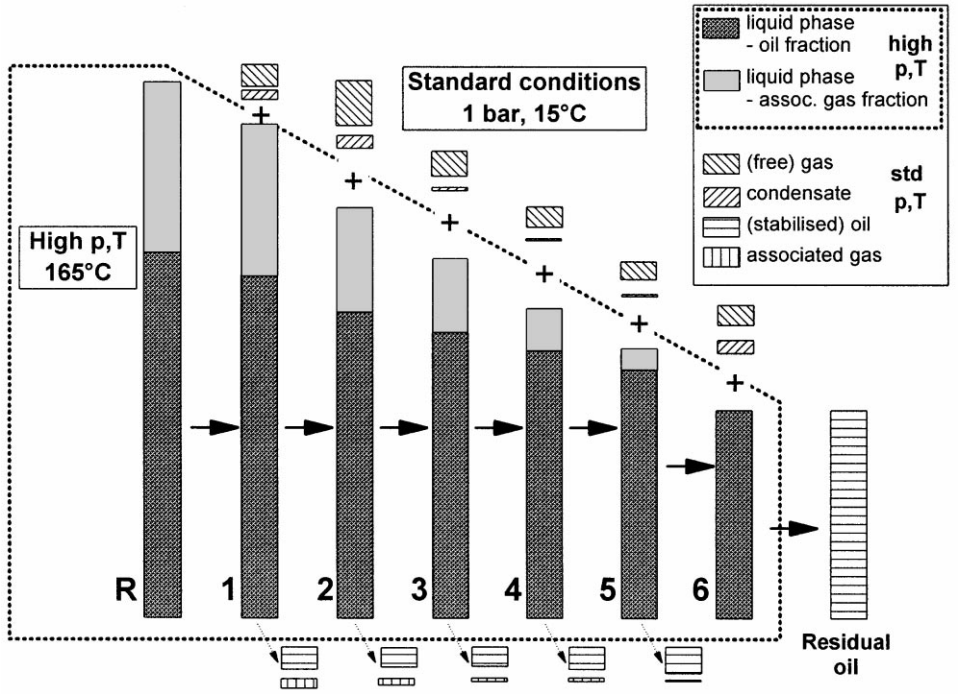

Fig. 2. Mass balance for differential evaporation experiment.

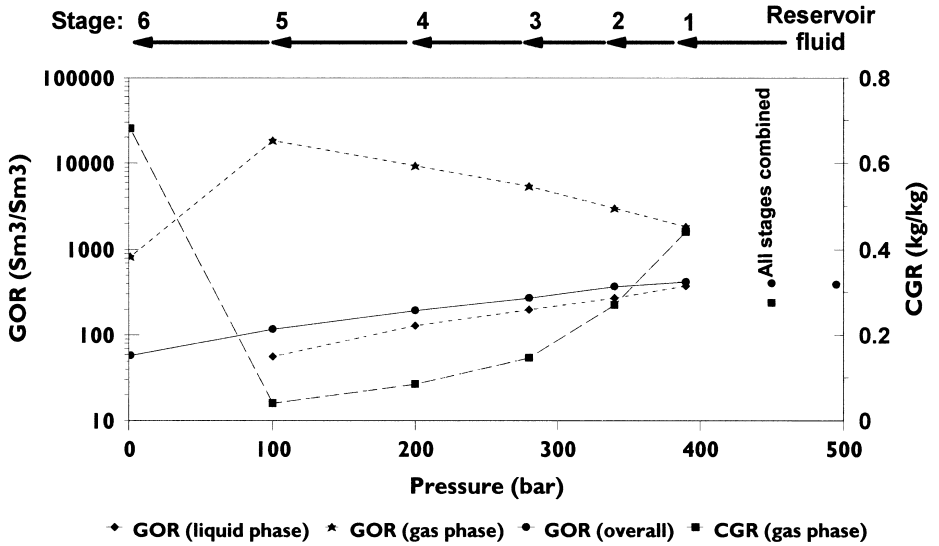

Fig. 3. Gas–oil ratio (GOR) for overall system, gas and liquid phases; condensate–gas ratio (CGR) for gas phase.

is not a geologically realistic situation (low pressure, high temperature).

The composition of the free gases changes relatively little during Stages 1 to 5, as this will largely be determined by the gas-condensate equilibrium at standard conditions. Only during Stage 6, when the condensate sample also changes significantly, the free gas is enriched in C_3–C_7 components. Throughout the experiment the associated gases become gradually enriched in C_2+ components. This is due to the preferential evaporation

Table 2
Differential evaporation experiment: bulk fluid composition, gas wetness[a] and Thompson indices[b]
a. Associated and free gases

	Associated gas						Free gas					
	S. Flash	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6
Composition (wt.%)												
N_2+CO_2	12.5	11.8	11.6	11.6	11.2	10.4	12.1	12.2	12.0	12.6	12.7	9.2
C_1	44.7	44.5	42.6	40.5	36.2	28.6	49.7	50.2	49.1	50.3	46.1	25.1
C_2	13.4	13.9	14.3	15.1	16.0	18.1	12.9	12.7	12.7	13.1	14.5	16.0
C_3	11.0	11.6	12.3	13.4	15.3	19.3	9.8	9.3	9.6	9.4	10.8	18.0
C_4[c]	7.7	8.1	8.8	9.5	10.9	13.5	6.5	6.1	6.4	5.8	6.7	14.6
C_5[c]	4.3	4.4	4.7	4.8	5.3	5.7	3.5	3.4	3.6	3.1	3.4	8.2
C_6[c]	2.4	2.3	2.3	2.2	2.3	2.0	2.1	2.1	2.3	1.9	2.0	4.1
C_7[c]	2.5	2.3	2.2	1.9	2.0	1.6	2.3	2.5	2.6	2.3	2.3	3.6
C_8+	1.6	1.1	1.1	0.9	0.9	0.7	1.1	1.6	1.7	1.6	1.5	1.2
Gas wetness	0.45	0.46	0.49	0.51	0.57	0.66	0.40	0.39	0.40	0.38	0.43	0.69
Thompson Indices												
A	0.35	0.32	0.30	0.30	0.28	0.26	0.30	0.32	0.31	0.32	0.32	0.31
B	0.87	0.68	0.67	0.66	0.65	0.63	0.61	0.74	0.72	0.74	0.72	0.54
X	0.44	0.25	0.33	0.55	0.37	0.00	0.22	0.34	0.29	0.27	0.25	0.23
C	1.08	1.15	1.19	1.24	1.19	1.28	1.14	1.11	1.10	1.08	1.09	1.29
I	1.95	2.13	2.13	2.11	2.08	2.07	2.19	2.22	2.21	2.22	2.20	2.10
F	0.58	0.63	0.63	0.62	0.59	0.60	0.65	0.68	0.68	0.68	0.68	0.66
H	16.5	16.4	16.4	15.3	15.3	14.8	17.4	18.8	18.8	19.2	19.0	15.3
U	1.16	1.14	1.11	1.08	1.08	1.04	1.17	1.20	1.20	1.22	1.20	1.06
R	1.72	1.63	1.61	1.51	1.52	1.47	1.67	1.85	1.85	1.92	1.91	1.49
S	20.4	18.1	17.5	16.4	14.7	12.9	20.1	22.2	21.3	22.4	21.7	18.1

b. Oils and condensates

	Oil							Condensate					
	S. Flash	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6
Composition (wt%)													
C_1–C_5	1.0	1.0	0.7	0.9	1.0	1.3	0.2	1.3	0.7	1.3	1.0	0.1	8.6
C_6[c]	1.1	1.1	1.0	1.1	1.1	1.1	0.3	1.5	1.4	2.0	1.8	0.5	9.4
C_7[c]	2.9	3.0	2.8	2.8	2.8	2.7	1.1	4.6	4.7	6.8	6.2	2.8	21.8
C_8[c]	4.9	5.1	4.6	4.5	4.3	4.1	2.4	8.9	9.9	15.1	14.7	8.4	27.7
C_9[c]	3.7	3.8	3.5	3.4	3.1	3.0	2.3	7.5	8.9	14.7	16.0	10.9	14.4
$C_{10}+$	86.4	86.1	87.4	87.4	87.8	87.8	93.7	76.2	74.4	60.1	60.3	77.3	18.2
Thompson Indices													
A	0.58	0.58	0.58	0.59	0.58	0.58	0.80	0.50	0.50	0.49	0.48	0.50	0.52
B	1.70	1.77	1.72	1.72	1.72	1.76	2.31	1.54	1.52	1.49	1.50	1.54	1.41
X	1.21	1.23	1.22	1.28	1.25	1.27	1.57	1.12	1.07	1.11	1.14	1.16	0.97
C	0.61	0.61	0.59	0.60	0.60	0.60	0.44	0.64	0.64	0.66	0.66	0.60	0.70
I	1.35	1.38	1.35	1.35	1.33	1.32	1.15	1.64	1.49	1.54	1.72	1.49	1.45
F	0.51	0.51	0.49	0.49	0.49	0.48	0.39	0.56	0.57	0.59	0.60	0.59	0.57
H	19.8	19.7	19.3	19.1	18.8	18.4	17.2	21.8	22.8	23.5	23.9	24.6	20.0
U	1.71	1.71	1.72	1.68	1.66	1.65	1.96	1.75	1.80	1.78	1.80	2.06	1.56
R	3.21	3.15	3.17	3.11	3.05	3.06	3.49	2.81	3.50	3.54	3.06	4.04	2.84
S	48.2	46.0	50.3	43.8	43.6	35.3	50.7	54.5	52.1	55.8	58.7	103	41.1

[a] Gas wetness = sum(C_2–C_5)/Sum(C_1–C_5).

[b] Thompson indices: C, (*n*-hexane + *n* heptane)/(cyclohexane + methylcyclohexane); U, cyclohexane/methylcyclopentane; A, benzene/*n*-hexane; I, (2- + 3-methylhexane)/Sum(dimethylcyclopentanes); R,*n*-heptane/2-methylhexane; B, toluene/*n*-heptane; R, *n*-heptane/methylcyclohexane; S, *n*-hexane/2,2-dimethylbutane; *X*, m/p xylene/*n*-octane; H, 100 * *n*-heptane/sum(heptanes) (chromatographically defined).

[c] "Pseudo-components" combining all peaks in a given elution range, e.g. C5 includes all material eluting after nC_4 up to and including *n*C5.

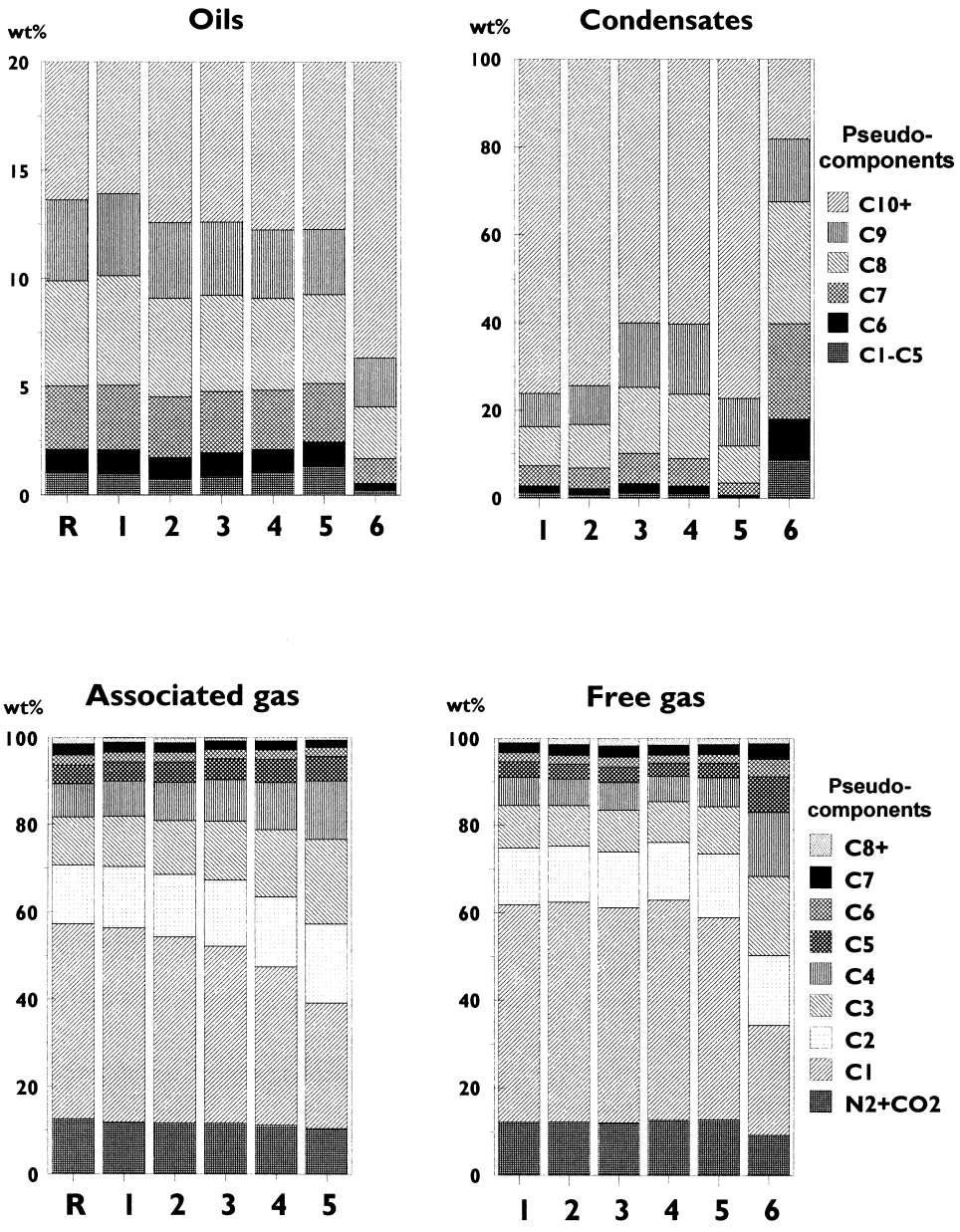

Fig. 4. Bulk composition of oils, condensates and gases.

of gas with a high methane content during each stage and the subsequent removal of the gas phases. Also here, the largest changes occur at the lower pressures.

Gas wetness [$\sigma(C_2–C_5)/\sigma(C_1–C_5)$; Table 2] is higher in associated gases than in free gases, as can be expected from a gas–liquid equilibrium. The wetness difference between the free and the associated gases is in agreement with the phase fractionation effect as described by Clayton (1991) in his gas classification plot of methane content vs. $\delta^{13}C$ of methane.

3.2. Gas isotope ratios

The $\delta^{13}C$ curves for methane through propane (Table 3, Fig. 5) show little change in the carbon isotope ratios from Stage 1 to 5 with no significant differences between the free and associated gases. The free gas from Stage 6 (no associated gas was released) is isotopically much heavier (12‰ for methane, 3‰ for ethane, 1.6‰ for propane) compared to the gases from the previous stages. The heavy isotopic signature of the Stage 6 free

gas could be the cumulative result of a small isotopic fractionation (with lighter isotopes preferentially in the gas phase) during each step, with the remaining dissolved gas becoming gradually heavier. The overall effect of this would be revealed during Stage 6 when the remaining amount of associated gas is converted into free gas (note that no associated gas is present at this stage). However, one would have expected to see a (small) difference between the isotope ratios in the free and the associated gases from the earlier stages and this is not the case. Unfortunately, no isotopic ratios could be obtained for the associated gas from Stage 5. These would be expected to have similarly heavy values as are observed in the free gas from Stage 6, as the associated gas in Stage 5 is the direct precursor of the free gas in Stage 6.

The $\delta^{13}C$ values in butanes (iso and normal) and in CO_2, and the $\delta^{18}O$ values in CO_2 show similar variations as observed for the $\delta^{13}C$ values of the C_1–C_3 hydrocarbons, with heaviest values in the Stage 6 gas and no systematic difference between the free and associated gases (Table 3). The δD values for methane show significant scatter but without a systematic pattern. Unlike the other isotope ratios, δD values are not heavier in the free gas from Stage 6.

The data clearly indicate that phase fractionation does not effect the gas isotope ratios, with the possible exception of fractionation at a very low pressure (1 bar, corresponding to a depth of 10 m), which removes the last remaining light components from the oil — a scenario that is not very likely to occur in nature. These results are in contrast to the work by Carpentier et al. (1996), who measured a phase fractionation effect in C_9–C_{14} *n*-alkanes and modelled that this also should be present in smaller molecules, even though this was not measured in C_6–C_8 *n*-alkanes.

3.3. Light hydrocarbon fraction (C_6–C_8)

A significant body of work on phase fractionation effects has been published by Thompson (1987, 1988, 1991). Thompson's efforts were concentrated on changes in the light hydrocarbon fractions, which were described in terms of "aromaticity", "paraffinicity" and "normality" via a suite of compound ratios, often referred to as Thompson Indices. As these concepts and ratios are commonly used in the geochemical literature, they will also be used here to describe the results of our differential evaporation experiment (Table 2).

The relative amount of aromatic compounds in the light hydrocarbon fraction compared to paraffins ("aromaticity") is described by Thompson indices A, B and X (see Table 2 for explanation). The variations in these parameters during the differential evaporation experiment are generally similar (Index B — toluene/nC_7 — is shown in Fig. 6): (i) fairly stable values in each fraction during Stages 1–5, (ii) higher ratios in liquid phases than in corresponding gas phases, both at high pressure and under standard conditions, and (iii) lower ratios in condensates than in corresponding oils. Only during the last stage, when the pressure is reduced from 100 to 1 bar (all at reservoir temperature 165°C), do the ratios change significantly and the difference between oil and condensate increases. Other light hydrocarbon parameters also display an anomalous behaviour during the last stage (see below). As discussed above, this is caused by the large mass transfer in this stage as a result of the — geologically unrealistic — combination of high temperature and low pressure.

The relative amount of paraffinic hydrocarbons (normal and branched) compared to naphthenic compounds ("paraffinicity"), as described by Thompson indices F, C, and I, also varies rather systematically during our

Table 3
Differential evaporation experiment: stable isotope ratios in free and associated gases[a]

	Associated gas						Free gas					
	S.Flash	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6
$\delta^{13}C$ (per mil vs PDB)												
Methane	44.4	44.2	44.4	44.1	44.4	n.m.[b]	44.4	44.2	44.3	44.3	44.4	32.1
Ethane	31.0	31.1	31.3	31.0	30.9	n.m.	31.1	30.9	31.0	31.2	30.8	27.6
Propane	28.8	28.6	28.7	28.8	28.9	n.m.	28.8	28.9	28.5	28.6	28.8	27.2
Isobutane	28.7	28.5	29.1	28.2	30.4	n.m.	28.4	29.1	28.8	28.0	27.9	27.5
n-Butane	28.6	29.2	29.0	28.8	28.9	n.m.	28.9	29.9	29.2	28.7	28.9	28.0
Carbon dioxide	14.2	14.5	14.8	15.0	14.4	n.m.	14.6	14.3	14.1	14.0	14.8	13.0
δD (per mil vs SMOW)												
Methane	208	230	208	222	229	n.m.	229	228	221	211	221	218
$\delta^{18}O$ (per mil vs SMOW)												
Carbon dioxide	14.4	14.6	14.6	14.2	12.9	n.m.	14.3	15.0	14.0	14.0	14.7	9.9

[a] The table also contains isotope ratios measured on a single flash reservoir gas.
[b] n.m.; not measurable due to small sample amount.

experiment (Index F- nC_7/methylcyclohexane — is shown in Fig. 7): (i) fairly stable values in all fractions during Stages 1–5, (ii) higher values in gas phases than in corresponding liquid phases, both at high pressure and under standard conditions, and (iii) higher values in condensates than in corresponding oils. Also here, the largest changes in the ratios occur during Stage 6.

Thompson Index H (nC_7 as% of chromatographically defined C_7-range) shows a more complicated pattern (Fig. 8): at elevated pressures and temperatures the gas phase has higher H values, while under standard conditions (15°C, 1 bar) liquids have higher values than corresponding gas samples. Condensates have higher values than oils. This behaviour illustrates clearly that both the

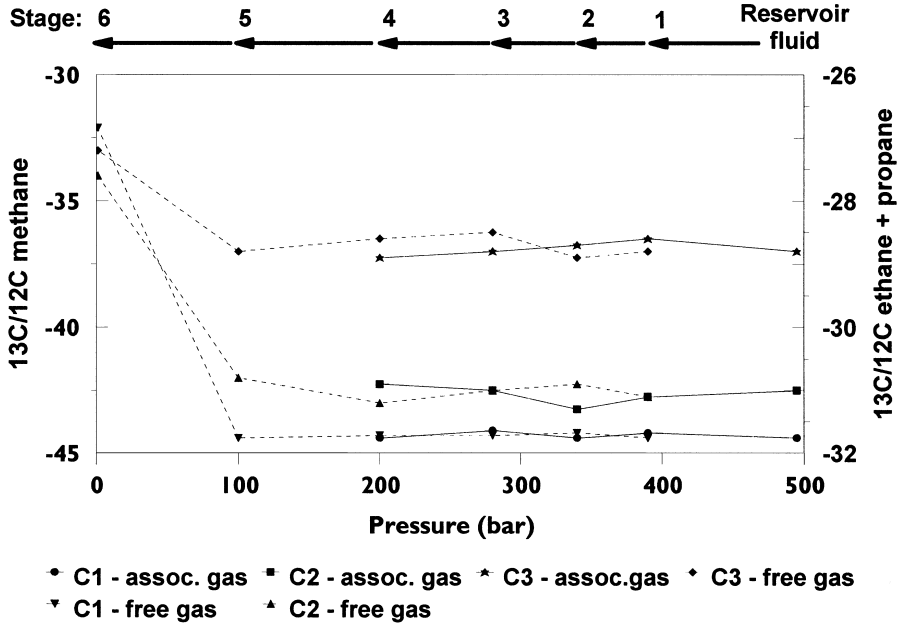

Fig. 5. $\delta^{13}C$ of methane, ethane and propane in free and associated gas.

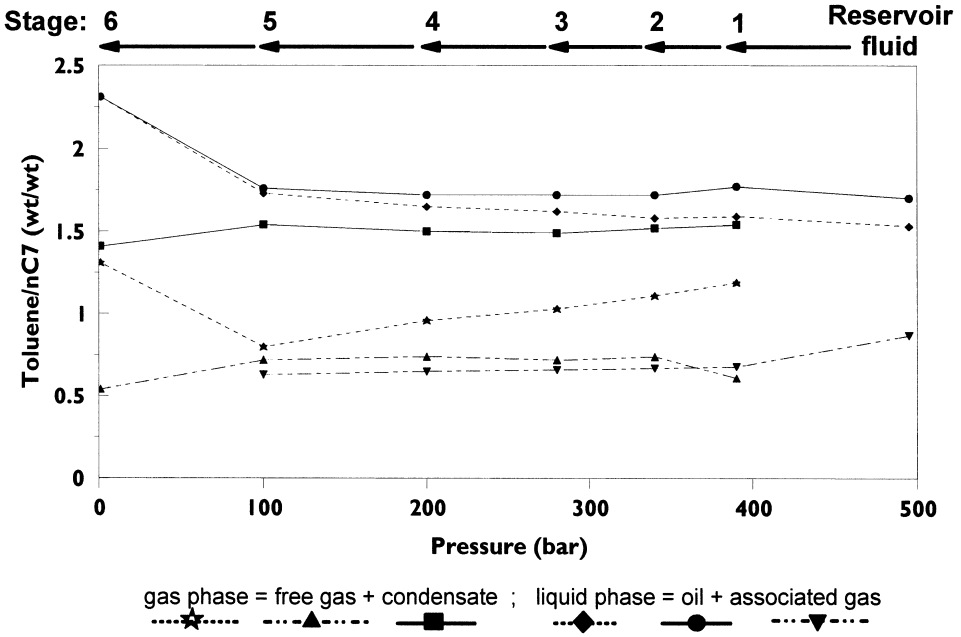

Fig. 6. Aromaticity: Thompson index B (toluene/*n*-heptane).

character and magnitude of phase fractionation effects will depend on the actual temperature and pressure of the system (in addition to the composition and relative amounts of both phases). One will have to be careful in constructing rules that have "universal" applicability.

The relative amount of normal compared to branched compounds ("normality") is described by Thompson indices U, R and S (Index R-nC$_7$/2-methyl-hexane — is shown in Fig. 9). As expected, gas samples are enriched in branched compounds (with lower boiling points),

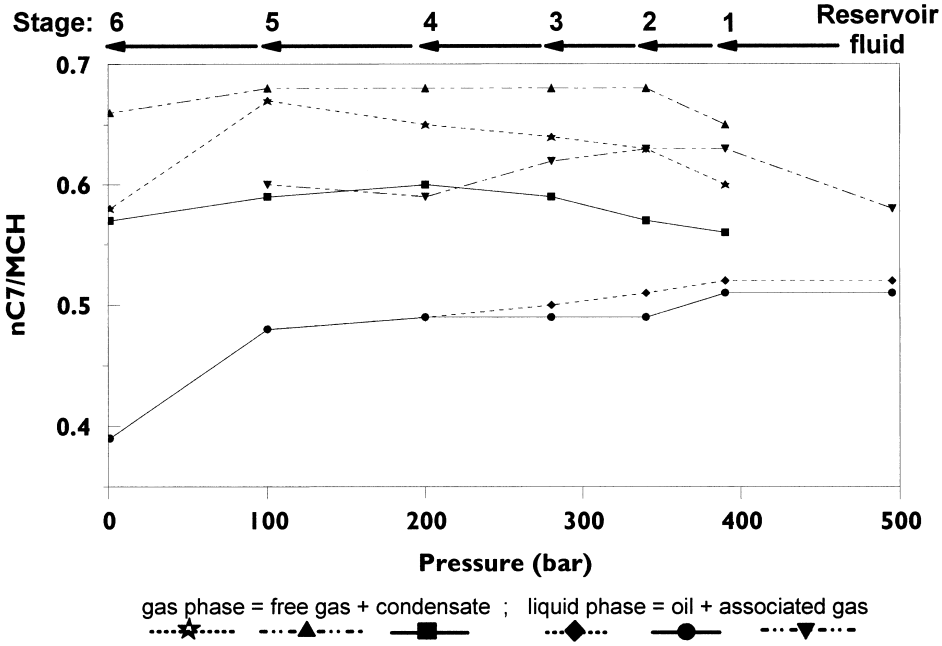

Fig. 7. Paraffinicity: Thompson index F (n-heptane/methylcyclohexane).

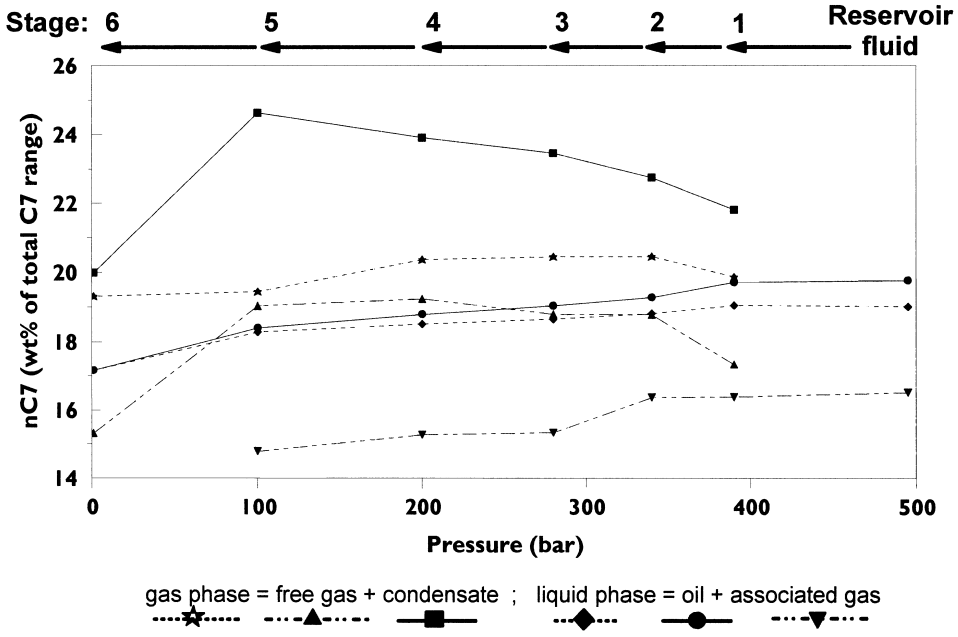

Fig. 8. Paraffinicity: Thompson index H (n-heptane as % of total C$_7$ components).

while the indices tend to be slightly lower in oils than in condensates, excluding the Stage 6 samples, where the condensate has lower values than the oil. This varying behaviour again illustrates the difficulty of establishing general rules for phase fractionation effects on individual geochemical parameters.

Thompson (1987) introduced a plot of Index F against Index B to recognise evaporative fractionation (and other

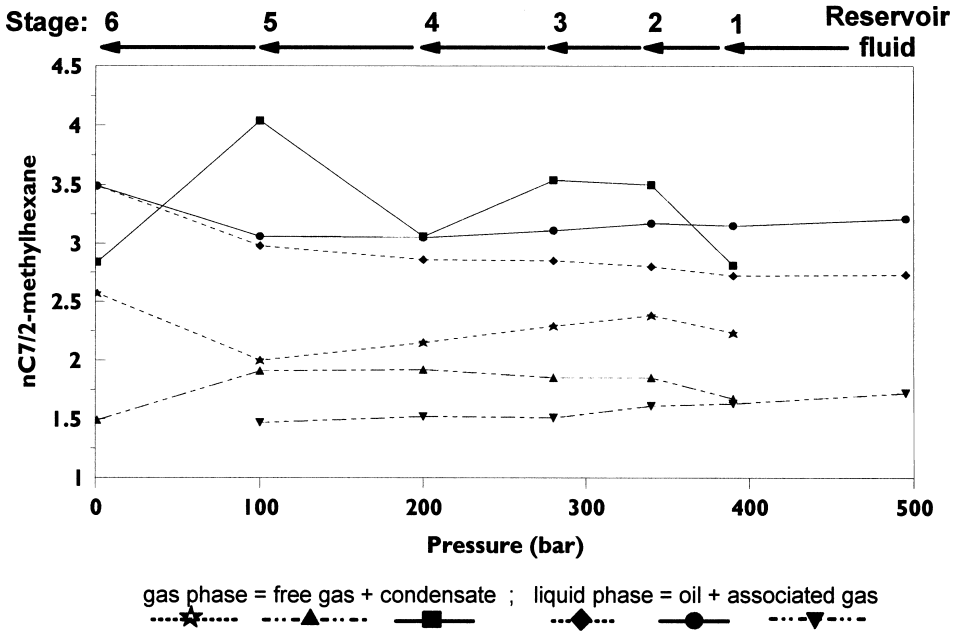

Fig. 9. Normality: Thompson index R (*n*-heptane/2-methylhexane).

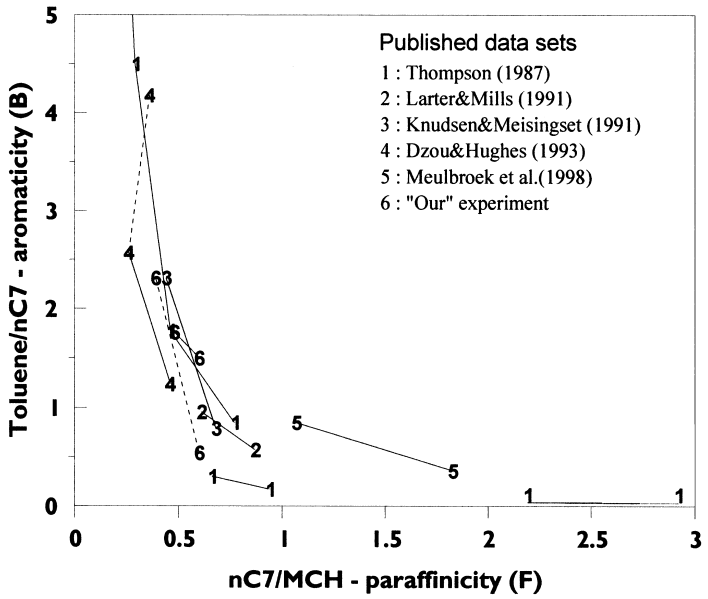

Fig. 10. Evaporative fractionation plot. (after Thompson, 1987). Data set for our experiment compared with literature data sets. Solid line for our data (b) indicates range for oils and condensates, excluding stage 6. Dashed line shows total range for all samples. For Dzou and Hughes (data set 4), the solid line shows the range of the most typical samples, while the dashed line also includes outliers.

Table 4
Differential evaporation experiment: gross composition and carbon isotope ratios of whole fluids and fractions

	Oils							Condensates					
	S.Flash	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6
Gross composition (wt.%)													
Saturates	76	78	77	78	78	80	75	85	83	80	78	76	75
Aromatics	20	17	20	18	17	16	20	13	16	17	16	21	18
Polars	3	4	2	3	3	3	3	2	1	2	6	3	7
Asphaltenes	0.4	1	1.2	0.9	1.3	1.1	2.4	0.1	0.2	0.4	0	0	0
$\delta^{13}C$ (per mil vs PDB)													
Whole fluid	27.8	28.1	28.7	28.4	28.2	28.3	28.1	28.5	28.4	28.4	27.9	n.d.[b]	28.2
Saturates	28.8	28.6	28.6	28.9	28.8	28.9	28.9	28.8	28.9	28.9	28.0[a]	28.7	28.4
Aromatics	27.3	27.4	27.2	27.3	27.3	27.2	27.3	26.9	26.9	27.2	27.3	28.8[a]	27.2
Polars	27.6	27.5	27.7	27.5	27.0	27.7	28.0	27.5	27.2	27.9	26.4	27.4	27.5
Asphaltenes	28.0	28.1	28.2	28.5	28.2	28.3	28.1	28.0	28.0	28.4	n.d.	n.d.	29.1[a]

[a] Unreliable due to small sample amount.
[b] n.d., not detectable.

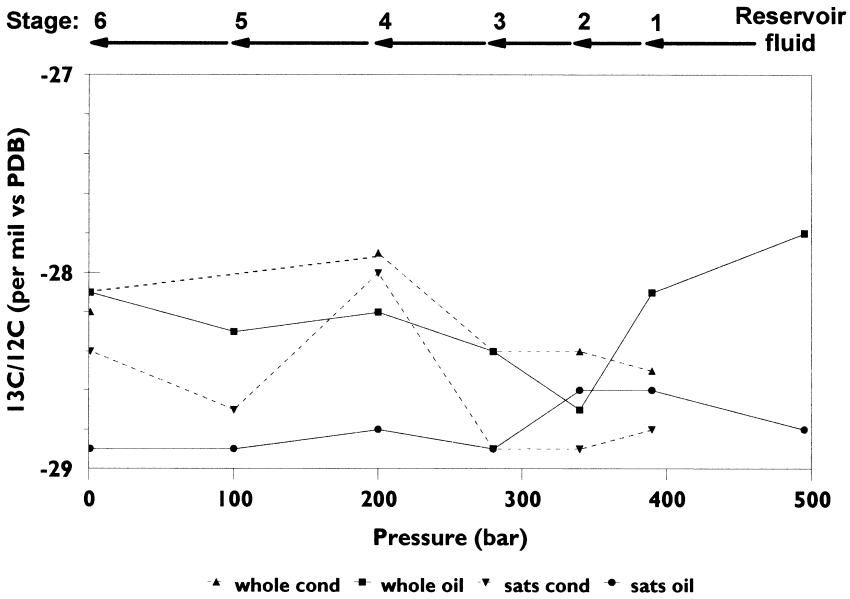

Fig. 11. $\delta^{13}C$ of whole fluids and saturated hydrocarbon fractions.

processes). Plotting our data in a similar way (Fig. 10) shows relatively small differences between oils and condensates, particularly after exclusion of the oil from the geologically unrealistic Stage 6. These results are similar to those reported by Thompson (1987) and Larter and Mills (1991) for single-step phase fractionations (see arrows in Fig. 10). Much larger fractionations were obtained by Thompson (1987) by repeatedly equilibrating an oil with large amounts of methane with subsequent removal of the gas phase and similar large variations were also observed in several natural systems (Dzou and Hughes, 1993; Meulbroek et al., 1998). While a scenario of repeated addition of gas to a reservoired oil may be realistic for the Gulf of Mexico, we believe that our relatively simple phase fractionation experiment without addition of excess dry gas is more applicable to the situation on the Norwegian continental shelf.

Overall, our observations on the C_6–C_9 hydrocarbons are qualitatively similar to those reported by others (e.g.

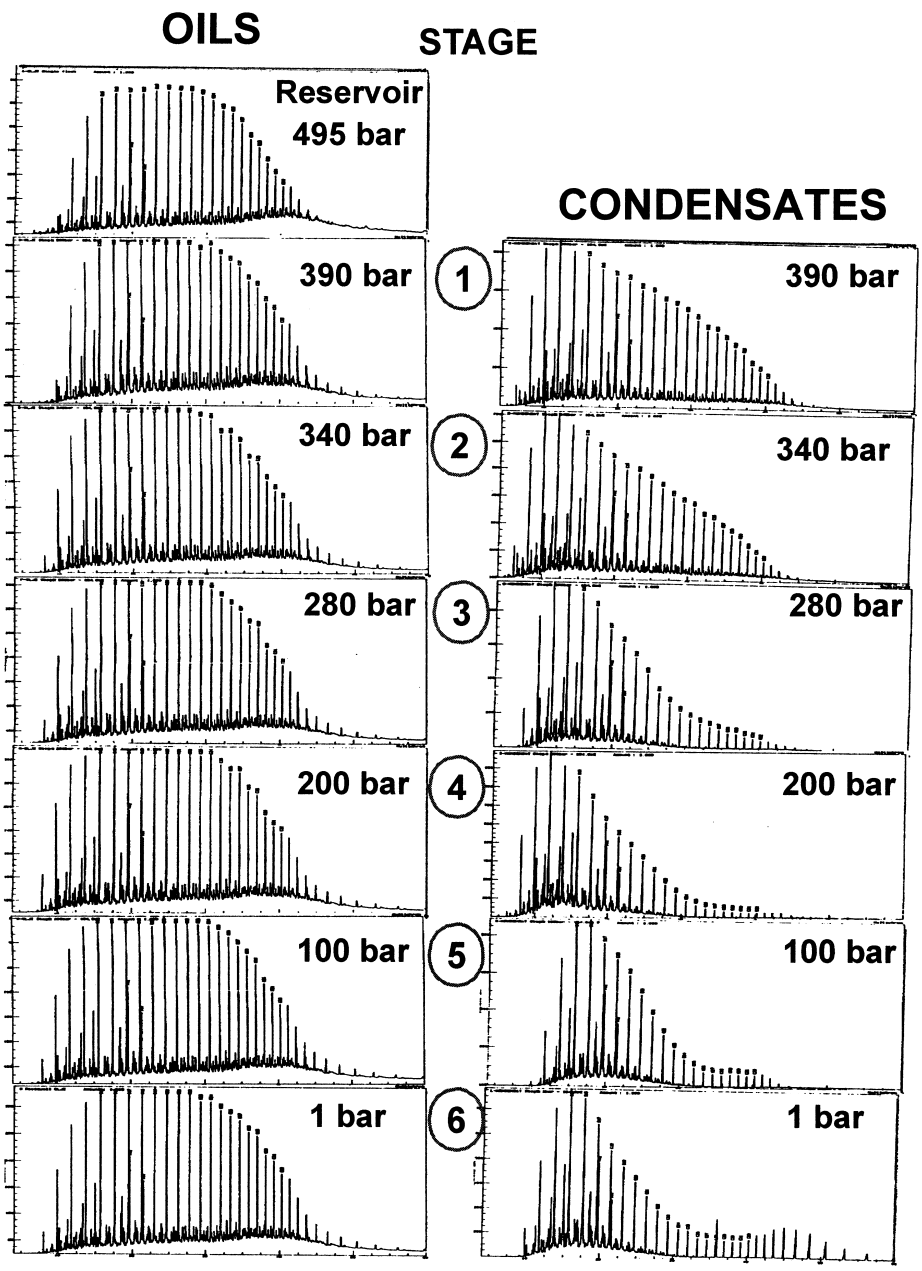

Fig. 12. Gas chromatograms of saturated hydrocarbon fractions from oils and condensates.

Thompson, 1987; Larter and Mills, 1991) with condensates having higher "paraffinicity" and lower "aromaticity" and "normality" than corresponding oils. Quantitatively, our oil-condensate differences are smaller than those found in the other studies, primarily reflecting the experimental design ("simple" phase equilibrium without addition of dry gas) and the composition of the starting fluid.

3.4. Gross composition of oils and condensates

The gross composition of the oil samples does not change much over the entire experiment (Table 4). In fact, the observed differences are generally in the same order as the reported uncertainty in Iatroscan data (approx.±1–2%; Bharati et al., 1997). Tentatively, condensate samples are slightly richer in saturated hydro-

Table 5
Differential evaporation experiment: GC and GCMS parameters from saturated and aromatic hydrocarbon fractions[a]

	Oils							Condensates					
	S.Flash	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6
Pristane/nC_{17}	0.62	0.65	0.63	0.63	0.63	0.63	0.62	0.64	0.71	0.74	0.71	0.71	0.69
Phytane/nC_{18}	0.43	0.44	0.44	0.43	0.43	0.47	0.43	0.43	0.44	0.49	0.46	0.47	0.44
Pristane/phytane	1.54	1.49	1.58	1.57	1.58	1.42	1.54	1.71	1.71	1.95	2.05	1.94	2.13
$nC_{17}/(nC_{17}+nC_{27})$	0.63	0.60	0.62	0.62	0.62	0.61	0.62	0.75	0.77	0.91	0.96	0.95	0.93
MSF (molar slope factor)	1.17	1.17	1.18	1.17	1.18	1.16	1.17	1.23	1.25	1.37	1.46	1.38	1.41
MPI1	0.71	0.69	0.65	0.71	0.73	0.71	0.65	0.68	0.68	0.67	0.62	0.65	0.64
20*S*	0.61	0.58	0.61	0.60	0.57	0.56	0.57	0.56	0.62	0.58	0.46	0.47	n.d.[b]
ββ	0.63	0.62	0.63	0.63	0.60	0.61	0.61	0.60	0.62	0.62	0.58	0.56	n.d.
T_s/T_m	4.56	4.19	4.35	3.89	4.64	4.00	4.31	4.86	4.54	3.27	n.d.	n.d.	n.d.
4*R*/3*R*	0.59	0.53	0.55	0.56	0.61	0.61	0.59	0.47	0.44	0.39	0.36	0.83	n.d.
27/29st	0.84	0.85	0.83	0.83	0.87	0.85	0.81	0.92	0.88	0.90	1.05	1.20	n.d.
3R/27dia	0.29	0.35	0.30	0.31	0.29	0.31	0.31	0.39	0.36	0.53	0.81	1.06	n.d.
Dia/reg	1.90	1.93	2.04	2.00	2.21	2.26	2.20	2.38	2.49	2.29	2.70	3.20	n.d.

[a] Molar Slope Factor (MSF) = molar concentration ratio of two successive n-alkanes, averaged for nC_{15} to nC_{25} (after Thompson, 1999a,b); MPI1 = 1.5*(3MP + 2MP)/(P + 9MP + 1MP); P = phenanthrene, MP = methylphenanthrene; 20*S* = 20*S*/20(*R* + *S*) 14α,17α-C_{29}-steranes; ββ = 14β,17β/(14β17β + 14α,17α) C_{29}-steranes 20(*R* + *S*); 4*R*/3*R* = C_{24}-tetracyclic terpane/C_{23}-tricyclic terpane; 27/29st = C_{27}/C_{29} 5α,14β,17β-steranes 20(*R* + *S*); 3R/27dia = C_{23}-tricyclic terpane/13β,17α-C_{27}-diasteranes 20(*R* + *S*); Dia/reg = 13β,17α-C_{27}-diasteranes 20(*R* + *S*)/14β,17β-C_{27}-steranes 20(*R* + *S*); measured in *m*/*z* 259 and *m*/*z* 218, respectively.
[b] n.d., not detectable.)

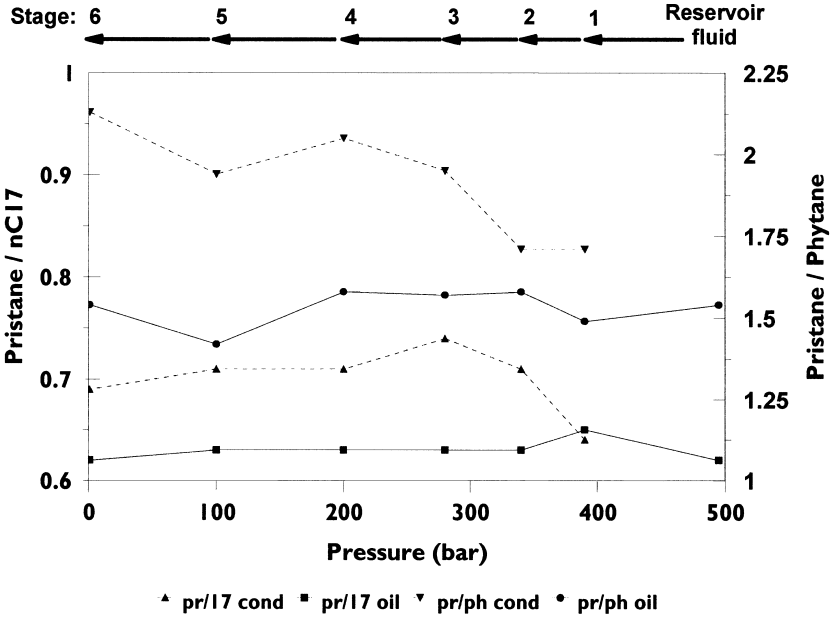

Fig. 13. Pristane/nC_{17} and pristane/phytane ratios in oils and condensates.

carbons (and correspondingly lower in aromatic hydrocarbons) during the earlier stages and gradually become more like the oils. This effect is in accordance with a higher "dissolving" power of the gas phase for long-chained ($>C_{20}$) paraffins at high pressures (see below). In general, our samples show less variation in gross composition data than those reported from other experiments; e.g. Larter and Mills (1991) found up to 10% enrichment of saturated hydrocarbons in their condensate samples.

3.5. Carbon isotope ratios of whole oils/condensates and fractions

$\delta^{13}C$ values for whole oils/condensates and their fractions (Table 4) show relatively small changes throughout the differential evaporation experiment. As a rule, the corresponding $\delta^{13}C$ values for oils and condensates are within 0.5‰ of each other, which is only slightly more than the analytical uncertainty, particularly with the small sample size that is the case for several of the condensate fractions.

The $\delta^{13}C$ values for the saturated hydrocarbons, which are probably the most reliable due to the larger size of this fraction, show an interesting pattern with lighter ratios in the condensates compared to the oils in Stages 1 and 2 and heavier condensates during the latter stages (Fig. 11). This pattern is in agreement with the change in the composition of the saturated hydrocarbon fraction (see below) with relatively more (isotopically light) long-chain alkanes in the condensate samples from Stages 1 and 2 and less in the later condensate samples. Note that the observed variations are small and in some cases come close to the uncertainty in the analytical data (normally <0.1‰, but can be larger in small samples).

Differences of max 0.5‰ between the isotopic ratios of whole fluids and fractions of oils and condensates, as observed in our experiments, would be considered as not significant in most correlation studies. However, Dzou and Hughes (1993) found isotopic shifts of up to 1.5‰ due to phase fractionation. These were caused by the very waxy nature of their oils and the resulting loss of isotopically light long-chain *n*-alkanes in the condensates, but if not recognised as phase effects, these differences could easily have been interpreted as indicating different sources for the oils and condensates.

3.6. $C_{15}+$ saturated hydrocarbons

The gas chromatograms of the saturated fractions from all oil samples (Fig. 12) are very similar and show a relatively large contribution of long-chain *n*-alkanes ($>C_{25}$). In the condensates, the amount of long-chain *n*-alkanes is slightly lower than in the oils during the first two stages at high pressures and this decreases rapidly at pressures below 300 bar (Stage 3 and onward). This clearly reflects a limited "solvent power" of the gas phase for longer chain molecules, as well as a decrease of this solvent power at lower pressures.

The lower solvent power of the gas phase for larger molecules at low pressures is also recognisable in the various parameters that are derived from the gas chromatograms (Table 5). Pristane/phytane ratios are slightly higher in condensates than in oils at high pressures, but this difference increases at lower pressures (Fig. 13). Note, that the Pr/Ph ratio of the oil does not decrease noticeably during the experiment, due to the small absolute quantities of pristane and phytane that are evaporated from the oil. As can be expected, the $C_{17}/C_{17}+C_{27}$ ratio shows higher values in condensates compared to oils, with an increase at lower pressures (Fig. 14). The stability of this ratio in the oil samples again illustrates the small amounts of these (relatively heavy) compounds that are evaporated.

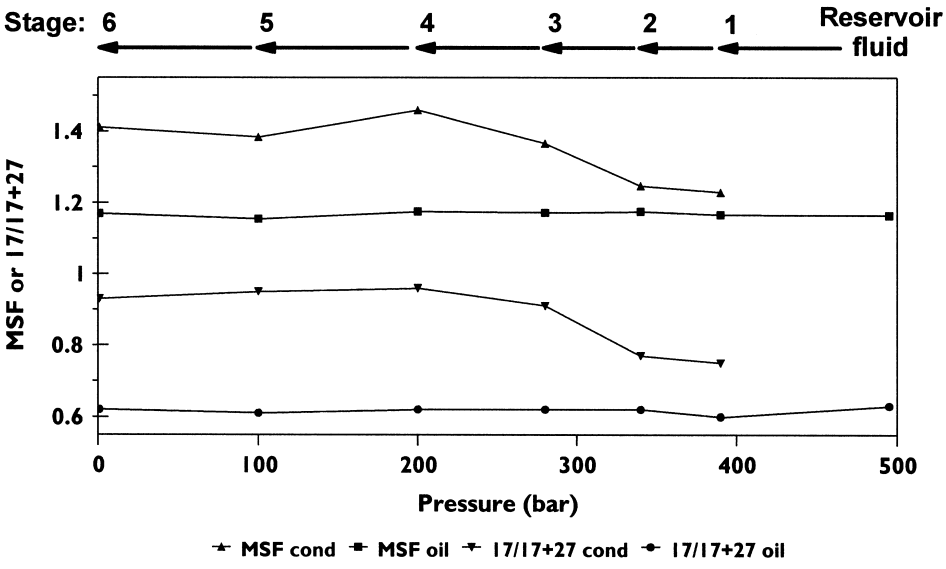

Fig. 14. Molar Slope Factor (MSF) and $C_{17}/(C_{17}+C_{27})$ ratio in oils and condensates.

Phytane/nC_{18} ratios are similar in oils and condensates (Table 5) and do not vary during the experiment. This is in line with the similar retention times (strongly dependent on boiling point) for both compounds. Somewhat surprisingly in view of the similar relative retention behaviour as phytane and nC_{18}, pristane/nC_{17} ratios are slightly but consistently higher in condensates than in oils for Stages 2 to 6 (Fig. 13). This illustrates the uncertainties in extrapolating boiling point differences (retention times) from standard conditions (1 bar, 15°C) to significantly higher temperatures and pressures.

Changes in the overall appearance of gas chromatograms as described above have also been reported by Thompson (1987, 1988), Larter and Mills (1991) and Knudsen and Meisingset (1991). Larter and Mills have also evaluated the Pr/Ph, Pr/nC_{17} and Ph/nC_{18} ratios,

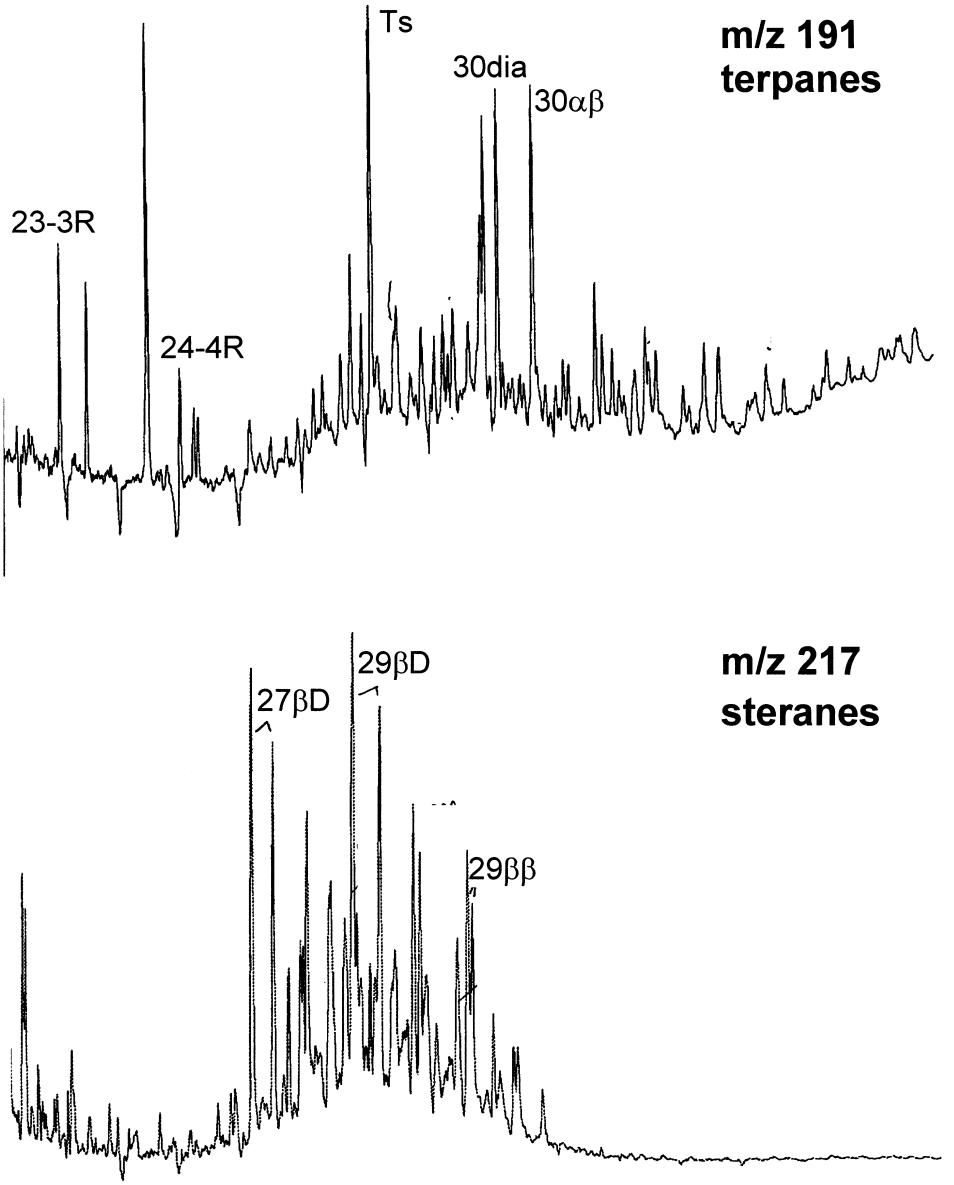

Fig. 15. Biomarker distributions (m/z 191 and m/z 217) in saturated hydrocarbon fractions from the starting reservoir oil. 23-3R = C_{23}-tricyclic terpane; 24-4R = C_{24}-tetracyclic terpane; T_s = 18α-22,29,30-trisnorneohopane; 30 dia = 15α(Me)-17α-27-norhopane; 30αβ = 17α,21β-hopane; 27 βD = 13β,17α-diacholestane; 29βD = 24-ethyl-13β,17α-dicholestane; 29 ββ = 24-ethyl-14β,17β-cholestane.

but unlike our results, they did not observe clear differences between oils and condensates. Higher Pr/Ph values for condensates compared to oils were reported by Dzou and Hughes (1993). In a study of samples from Vermilion 39, Curiale and Bromley (1996) identify two groups of samples and attribute the differences between the groups to migration fractionation processes. These differences include variations in the total gas chromatograms, similar to those found in our experiments, and significantly higher Pr/Ph ratios (shift from 2–2.5 to 3–4.5) in fractionated samples.

In work on oils and condensates from the Gulf of Mexico, Thompson (2000a,b) introduced the so-called Molar Slope Factor (MSF) as a measure of the decrease

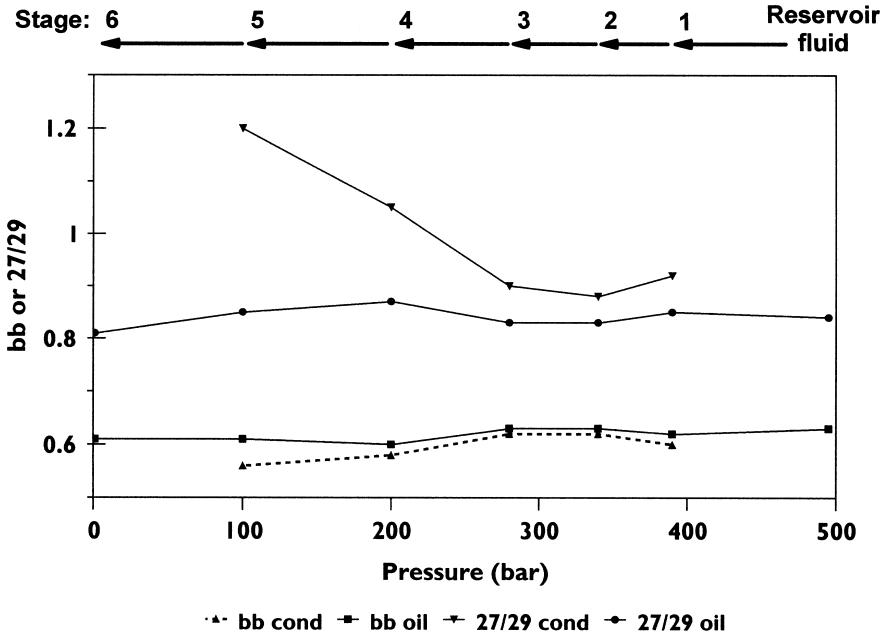

Fig. 16. 14β,17β/(14β,17β + 14α,17α) C_{29} steranes (bb) and C_{27}/C_{29} 14β,17β-steranes (27/29) in oils and condensates.

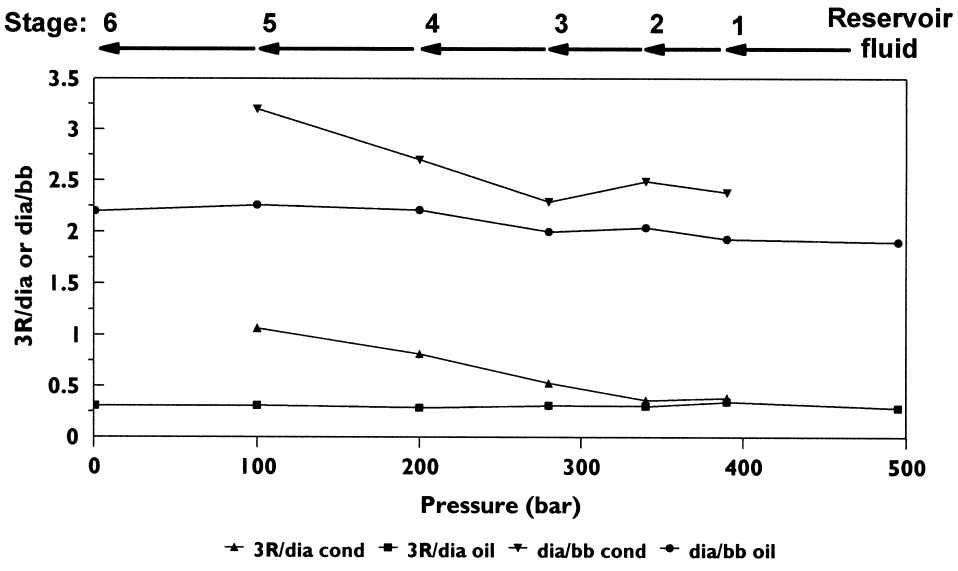

Fig. 17. C_{23}-tricyclic terpane/C_{27}-diasteranes (3R/dia) and C_{27}-diasteranes/C_{27}-14β,17β-steranes (dia/bb) in oils and condensates.

in *n*-alkane concentrations with increasing chain lengths that normally occurs in mature marine oils.[4] According to Thompson's results "normal" oils have slope factors lower than 1.2, with thermal condensates having slope factors of approximately 1.2 and evaporative condensates having substantially higher values. Our data are in agreement with this (Fig. 14) with constant slope factors in the oils (1.16–1.17) and significantly higher values in the corresponding condensates (1.23–1.46), particularly at lower pressures (< 300 bar). This supports Thompson's suggestion that the MSF can be a useful tool in the classification of oils and condensates.

The reservoir fluid used in our experiment has a relatively high maturity (deep end of the oil generation

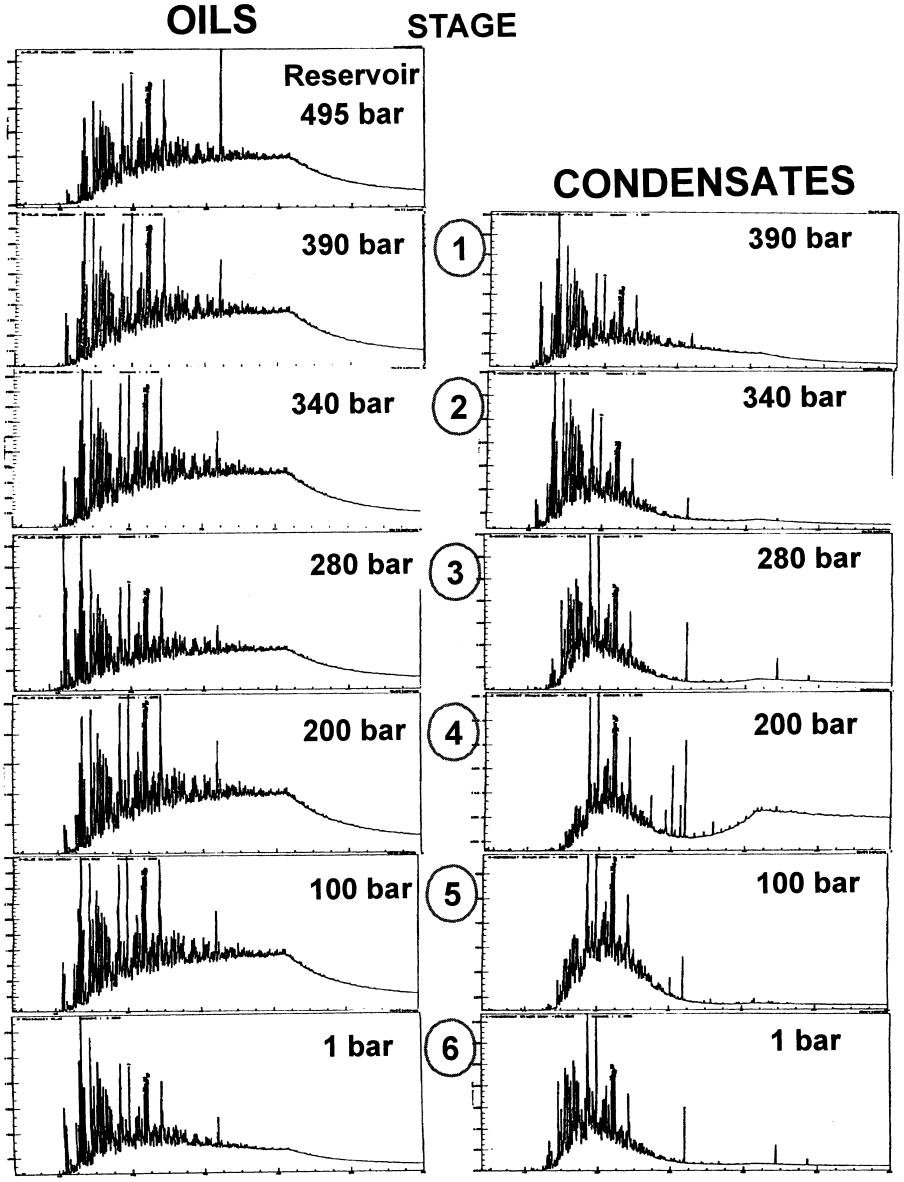

Fig. 18. Gas chromatograms of aromatic hydrocarbon fractions from oils and condensates.

[4] According to Kissin (1987) the logarithmic molar concentrations of n-alkanes in petroleum are linearly related to their carbon number. In such a plot, the slope factor would express the angle of the straight line. As used in this paper, the MSF is equal to the molar concentration ratio of any pair of adjacent alkanes: the MSF = $[n]/[n+1]$. By averaging individual values, slope factors can be calculated for different carbon number ranges (see Table 5).

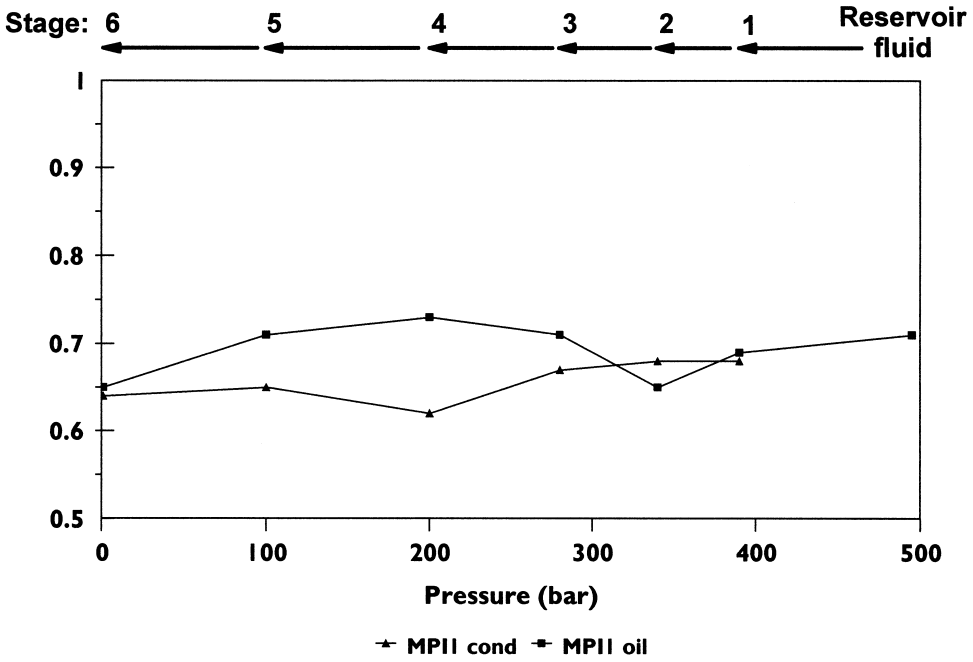

Fig. 19. Methylphenanthrene index (MPI1) in oils and condensates.

window), which is clearly reflected in the biomarker distributions (high diasteranes, T_s/T_m and diahopane; see Fig. 15). The quality of the GCMS data for the saturated hydrocarbon fractions is generally good with the exception of the condensate samples from Stages 4–6 which have very low biomarker concentrations and correspondingly poor signal/noise ratios, particularly in case of the triterpanes. Only a few biomarker compounds could be detected in those samples (none in the condensate from Stage 6).

In general, smaller molecules are enriched in condensates compared to oils and individual biomarker parameters are affected accordingly. Ratios calculated from molecules of different size or from isomers with a different retention behaviour, such as C_{23} tricyclic terpane/C_{27} diasteranes, C_{27}/C_{29} ββ-steranes or dia/ββ C_{27} steranes, show fairly similar values in oils and condensates at high pressures but increasingly higher values in condensates at lower pressures while the values in oils remain unchanged (Figs. 16 and 17). In contrast, a ratio composed of more similar molecules, like ββ/(αα + ββ) C_{29} steranes (Fig. 16), has similar values in oils and condensates throughout the entire experiment. Depending on the pressure, several biomarker ratios will show differences between coeval oils and condensates that could easily lead to erroneous conclusions in correlation studies if not recognised as being induced by phase fractionation. This conclusion was also reached by Curiale and Bromley (1996), who observed variations in biomarker distributions very similar to those seen in our samples.

3.7. $C_{15}+$ aromatic hydrocarbons

The gas chromatograms of the aromatic hydrocarbon fractions from all oil samples (Fig. 18) are rather similar, as is the case for the saturated hydrocarbon fractions. The differences that can be observed, are probably mainly due to variations introduced during the solvent evaporation steps where a variable amount of the low-boiling compounds (C_1- and C_2-naphthalenes) can be lost. More variation is seen amongst the condensate samples. In general, condensates differ from oils in having a lower Unresolved Complex Mixture (UCM) hump at high retention times. As in the case of the saturated hydrocarbons, this difference is more pronounced at lower pressures, when the solvent power of the gas phase for these relatively large aromatic compounds is greatly reduced.

Inspection of the behaviour of an important aromatic maturity parameter, the methyl- phenanthrene index (MPI1; Radke, 1988), shows generally slightly higher values in oils than in condensates (Fig. 19). However, the differences are small and of the same magnitude as the analytical uncertainty. This is due to the way in which the MPI1 is calculated with the compounds in the

numerator (3- and 2-methylphenanthrenes) having an intermediate GC-retention time behaviour compared to the compounds in the denominator (phenanthrene and 9- and 1-methylphenanthrenes). Insignificant variations in MPI1 values were also reported by Larter and Mills (1991) and Dzou and Hughes (1993). In contrast, Thompson (1991) did report significant differences between oils and condensates as a result of phase fractionation, but in his case the fractionation conditions were much more severe.

Due to the relatively high maturity of the reservoir fluid that was used in our experiments none of the samples contains detectable amounts of C_{26}–C_{29} mono- or triaromatic steroid hydrocarbons.

4. Conclusions

In a six-stage differential evaporation experiment only small variations were observed in the composition of the oil samples. This is largely due to the composition of the starting fluid (gas–oil ratio 400 Sm^3/Sm^3), giving a quantitative dominance of the liquid phase throughout the experiment.

The compositions of the evolved free and associated gases vary as can be expected, with the associated gas being wetter than the free gas and becoming increasingly wet at lower pressures. Carbon isotope ratios of C_1–C_4 hydrocarbons show no significant differences between the free and associated gases.

Changes observed between the light hydrocarbon (C_6–C_9) fractions of the oils and condensates are similar to those reported by other workers (e.g. Thompson, 1987) with oils having lower ''normality'' and higher ''aromaticity'' and ''paraffinicity'' than the corresponding condensates. Careful evaluation of the data shows that not only the magnitude of phase fractionation effects is dependent on temperature and pressure, but also that the direction of fractionation effects (i.e. if parameters increase or decrease) may change when going from high temperature and pressure to standard conditions (15°C, 1 bar).

Evaluation of the saturated and aromatic hydrocarbon fractions in condensates shows that the gas phase has a good solvent power for large ($>C_{20}$) molecules at high pressures (>300 bar), which is considerably reduced at lower pressures. Differences between oils and condensates for individual parameters are very much as can be expected from molecular size (boiling point, GC-retention time) of the compounds involved, with smaller molecules being preferentially enriched in the condensates. Phase fractionation effects on several geochemical parameters can be sufficiently large to interfere with a ''simple'' correlation between oils, condensates and source rocks.

In general, it will be very difficult to set up detailed guidelines for how individual geochemical parameters will change due to phase fractionation, since these will be controlled by a complex set of parameters: (i) pressure and temperature of fractionation, (ii) composition of the fluids involved, e.g. API gravity of the oil, composition of the gas, and (iii) relative amounts of oil and gas in the system (gas–oil ratio of a single-phase petroleum, amount of gas added to an oil-filled reservoir). Different petroleum fractions (and their derived parameters) will be affected most strongly depending on the specific conditions under which phase fractionation occurs.

In summary, the results obtained from our experiments further support the importance of phase fractionation as an important process to consider when interpreting geochemical data for both condensates and oils.

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